First-principles investigationofdefectsatGaAs/oxideinterfaces

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Abstract

First-principles calculations of the ESR parameters of several point defects at GaAs/oxide interfaces and in bulk $GaAsO_4$ are reported. Comparing the theoretical results with recent experimental data, obtained from ESR experiments on thermally oxidized GaAs surfaces, we first confirm the formation of As antisite defects at the GaAs/oxide interface during its thermal oxidation. Two other ESR active defects, which were not identified so far, are tentatively assigned to an As vacancy in the oxide and to a As dangling bond, backbonded to two O atoms and one As atoms, also present in the GaAs oxide layer. The formation of these oxide defects could be correlated to the As enrichment of the GaAs interface during its thermal oxidation.

1. Introduction

As the scaling of advanced metal–oxide–semiconductor field effect transistors (MOSFETs) is approaching its technological and fundamental limits, new materials are required to further improve the performances of these devices. Among these materials, high mobility semiconductors, like Ge and III–V compounds are investigated as potential replacements of the Si channel [1], [2], [3], [4] and [5]. A major issue common to III–V compounds like GaAs, InGaAs and InP is the passivation of their interfaces, i.e. achieving a sufficiently low density of interface (or near interface) defects at III–V/oxide interfaces, comparable to device-grade Si/SiO_2 interfaces (after forming gas annealing), with interface defect densities typically below $10^{10}/cm^2$. Most III–V/oxide interfaces present a much larger defect density, typically in the 10^{12}–$10^{13}/cm^2$ range [1], [2], [3], [4] and [5]. Identifying these defects might help in improving growth processes to reduce their densities and/or to passivate these defects. Theoretical calculations on several possible defects at III–V surface and III–V/oxide interfaces have been recently reported [6], [7], [8], [9] and [10], these theoretical works focusing on the formation energies and position of the defect levels in the energy band gap of the III–V compound.

In an attempt to gain fundamental insights into III–V/oxide interface defects, multi-frequency electron spin resonance (ESR) experiments on GaAs/(thermally grown) oxide interfaces have been recently reported [11] and [12], ESR being the spectroscopic technique of choice for the characterization and atomic identification of paramagnetic defects. These experiments revealed the presence of several ESR active defects at GaAs/oxide interfaces, among which most likely

the As antisite defect (As_{Ga}^{+}AsGa+) with g=2.043 and hyperfine coupling constant A_{iso}=910 G. Two other defects, with g=2.063 and g=1.937, most likely present in the GaAs oxide layer, have still not been identified.

We report here the results from first-principles calculations of the ESR parameters of point defects at GaAs/oxide interfaces and in $GaAsO_4$. Comparing the computed g-values with the experimental results, we tentatively assign the defect with g=2.063 to an As vacancy in the oxide, and the g=1.937 defect to a dangling bond localized on an As atom, backbonded to two O atoms and one As atom.

2. Computational details

First-principles calculations were performed on atomic cluster models, using the B3LYP hybrid exchange-correlation functional [13], as implemented in the full-electron ORCA code [14]. Spin-unrestricted DFT calculations were performed, using the 6-311 G(d,p) gaussian-type basis sets [15], all electrons being explicitly treated relativistically. Convergence tolerances in the geometry relaxation of the cluster models were fixed to $3\times10^{-4}E_h$(hartree)/bohr for the gradient and $5\times10^{-6}E_h$ for the total energy, using a 300 point grid for the numerical integrations. The g-matices and hypefine coupling tensors were computed on relaxed structures, from the second derivative of the energy of the system in presence of a magnetic field perturbation, as implemented in ORCA [14].

3. Results and discussion

We first calculated the ESR parameters of a As_{Ga}^{+}AsGa+ antisite defect present near a GaAs/oxide interface model, as shown in Fig. 1. This GaAs/oxide cluster model (92 atoms) was obtained from molecular dynamics simulations of the oxidation of (001)GaAs β2(2×4) in O_2, as discussed in more details elsewhere [16] and [17]. The dangling bonds at the outer atoms of the cluster were passivated by H-atoms, as required for simulations performed using non-periodic boundary conditions. Note that the generated GaAs/oxide interface model shows a preferential oxidation of the Ga atoms (about 65% of Ga atoms are present in the oxide layer), consistent with experimental results pertaining to thermally oxidized GaAs surfaces [18] and [19]. Note also that a large fraction of Ga (about 40%) and As (about 65%) atoms in the oxide layer are in a +3 oxidation state (forming bonds with three O neighbors), also in agreement with experimental results [19].

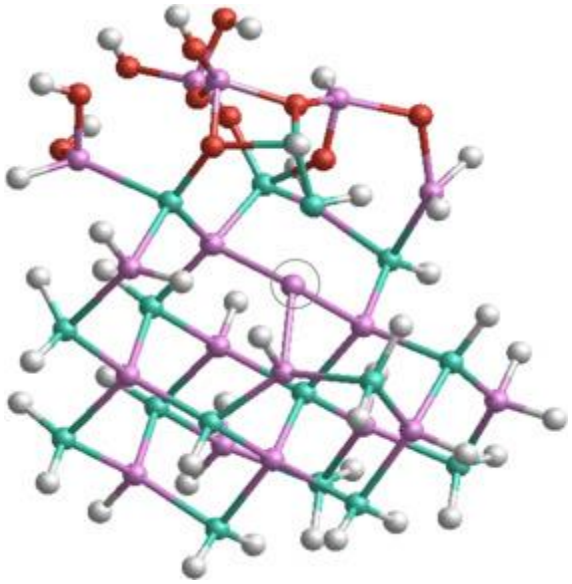

Fig. 1.

As antisite defect (As_{Ga}AsGa+) present near the GaAs/oxide interface model. The As antisite is circled. Green, magenta, red and white spheres are Ga, As, O, and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure options

A positively charged As antisite was generated at the GaAs/oxide interface. After structural relaxation, the average As–As bond length at the antisite is calculated to be about 2.59 A, in very good agreement with previous theoretical calculations (2.58 A) [20]. The computed *g*-values and A_{iso} for this defects are 2.031 and 824 G, respectively. These values are in good agreement (within typically 5%) with previous DFT calculations performed on a GaAs cluster model [21]. These values are also in fair agreement with those observed from the ESR experiments on GaAs/oxide interfaces (g=2.043 and A_{iso}=910 G), confirming that this defect is likely the positively charged As antisite, produced during the thermal oxidation of the (100)GaAs surface.

We next calculated the *g*-values of several defects, like O (V_O), As (V_{As}) or Ga (V_{Ga}) vacancies, and As ($O_3{\equiv}As^{\bullet}O3{\equiv}As\bullet$) or Ga ($O_3{\equiv}Ga^{\bullet}O3{\equiv}Ga\bullet$) dangling bonds present in a bulk $GaAsO_4$ cluster model (60 atoms); this atomic cluster was build from an α-quartz $GaAsO_4$ periodic structure [22]. The computed lattice parameters of the relaxed $GaAsO_4$ unit cell are a=b=4.923 Å, c=11.799 Å, α=β=90° and γ=120°; the computed Ga–O and As–O bond lengths are 1.91 and 1.75 Å, respectively, within about 2–3% as compared to a previous theoretical work [22].

The computed isotropic *g*-values of O, As and Ga vacancies are summarized in Table 1. Very interestingly, we found that g_{iso} of an As vacancy in $GaAsO_4$ (as illustrated in Fig. 2) is about 2.05, close to the ESR signal with g_{iso}=2.063. Since the thermal oxidation of GaAs is supposed to lead to the enrichment of the As atoms near the GaAs/oxide interface [18] and [23], the presence of As vacancies in the oxide can be expected.

Table 1.

Computed isotropic *g*-values of different defects in the $GaAsO_4$ atomic cluster model.

Defect	g_{iso}
V_O	2.002
V_{Ga}	2.019
V_{As}	2.051
$O_3{\equiv}Ga^{\bullet}O3{\equiv}Ga\bullet$	2.005
$O_3{\equiv}As^{\bullet}O3{\equiv}As\bullet$	1.998
$AsO_2{\equiv}As^{\bullet}AsO2{\equiv}As\bullet$	1.962

Table options

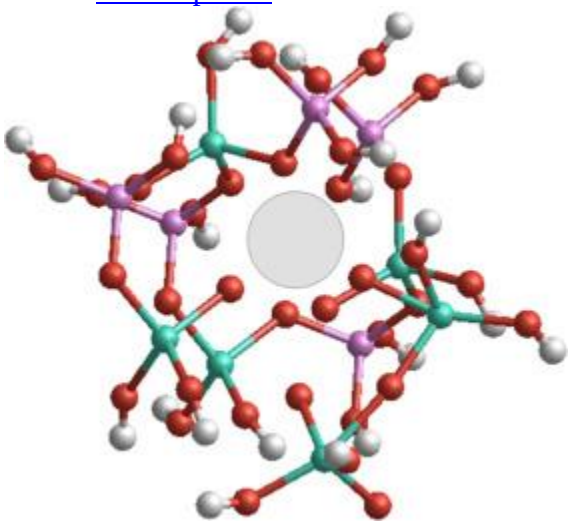

Fig. 2.

As vacancy present in the $GaAsO_4$ cluster model. The shaded area corresponds to the position of the vacant As atom. Green, magenta, red and white spheres are Ga, As, O, and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure options

The computed isotropic *g*-values of dangling bonds localized on Ga and As atoms are 2.005 and 1.998, respectively (see Table 1). These values are not consistent with the ones related to the observed ESR signal with g_{iso}=1.937. Interestingly, one specific defect has a computed g_{iso}=1.962, which is the closest one we found with respect to the observed ESR signal. This defect corresponds to a dangling bond on an As atom in $GaAsO_4$, with two O backbonds and one As backbond ($AsO_2{\equiv}As^{\bullet}AsO2{\equiv}As\bullet$ center), as shown in Fig. 3. This defect, possibly present close to the GaAs/oxide interface, could also be related to the As enrichment of the interface during its oxidation (due to the presence of the As–As backbond), as also pointed out by molecular dynamics simulations on GaAs/oxide interfaces [16], highlighting the ejection of Ga

atoms in the oxide (and formation of As–As bonds at/near the inerface), as a mechanism for the release of interface stress induced by the oxidation of the GaAs surface.

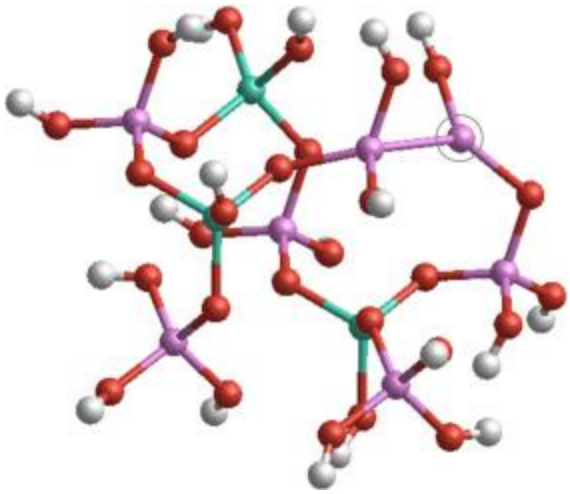

Fig. 3.

$AsO_2{\equiv}As^{\bullet}$AsO2≡As● center present in the $GaAsO_4$ cluster model. The As atom with the dangling bond is circled. Green, magenta, red and white spheres are Ga, As, O, and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure options

4. Concluding remarks

In summary, comparing recent experimental ESR spectra observed on GaAs/(thermal) oxide interface with first-principles simulations performed on atomic cluster models, we first confirmed the likely formation of As antisites at the GaAs/oxide interface during its thermal oxidation, producing a defect level with g_{iso}=2.043 and hyperfine coupling constant A_{iso}=910 G, as compared to the computed values g_{iso}=2.031 and A_{iso}=824 G, respectively, for the positively charged As antisite (As^{+}_{Ga}AsGa+). Next, we tentatively assigned two other (oxide) defects observed by ESR, the one with g_{iso}=2.063 being possibly an As vacancy in the oxide (computed g_{iso}=2.051), and the one with g_{iso}=1.937 being assigned to a $AsO_2{\equiv}As^{\bullet}$AsO2≡As● center (computed g_{iso}=1.962), both defects being present in the oxide layer, possibly close to the interface. The formation of these oxide defects could be correlated to the As enrichment of the GaAs interface during its thermal oxidation.

Acknowledgments

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